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Investigations into the Polyaniline and Polypyrrole Families of Conducting Polymers for Application as Radar Absorbing Materials

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University of Victoria Co-op Student

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Abstract

The synthesis and characterization of two families of conducting polymers, namely polyaniline and polypyrrole, were investigated in order to ascertain their viability as radar absorbing materials (RAM). A large number of polyanilines (including derivatives and copolymers) were synthesized by chemical oxidative polymerization, while the polypyrroles were produced by electrochemical oxidation. The syntheses were performed under varying reaction conditions (variable temperature, time, dopant, oxidant/monomer ratio) to investigate the effects of the synthetic parameters on the conductivity and permittivity of the resulting polymers. The conductivity of the polymers was measured using the four point probe method at ambient temperature. In the case of polyaniline, the samples were either pressed pellets of the bulk polymer or polyaniline/acrylic composites, whereas the polypyrrole samples were in the form of thin films. The complex permittivity of the polymers was determined from the reflection parameters measured across the X-band (8 - 12 GHz) in the microwave region of the electromagnetic spectrum. The data indicate that the synthetic parameters investigated, do indeed have an effect on the morphology of the polymers, and thus on the conductivity and permittivity.

Résumé

Nous avons étudié la synthèse et la caractérisation de deux familles de polymères conducteurs — les polyanilines et les polypyrolles — afin d'établir leur utilité comme matériaux antiradar. Nous avons synthétisé un grand nombre de polyanilines (ainsi que leurs dérivés et leurs copolymères) et de polypyrolles, respectivement par oxydo-polymérisation chimique et oxydation électrochimique. Afin d'étudier les effets des paramètres de préparation sur la conductivité et la permittivité des polymères produits, nous avons réalisé ces synthèses dans différentes conditions de réactions (température, temps, dopant, rapport oxydant-monomère). Les échantillons de polyaniline étaient constitués de boulettes compressées de polymère en vrac ou de composites polyaniline-acrylique, tandis que les échantillons de polypyrolles étaient formés de pellicules minces. Nous avons mesuré la conductivité des polymères à la température ambiante, avec la méthode quatre pointes et leur permittivité complexe, à partir des paramètres de réflexion de signaux dans la bande X du spectre électromagnétique (dans la région des micro-ondes, entre 8 et 12 GHz). Nos données indiquent que les paramètres de préparation étudiés ont un effet sur la morphologie des polymères et, donc, sur leur conductivité et leur permittivité.

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Executive summary

Introduction

Traditional radar absorbing materials (RAM), such as ferrites or carbon black, are fraught with problems relating to their integrity. These substances must be incorporated into a matrix in order to be useful, however, poor adhesion with the matrix material results in sloughing, and therefore loss of the material, requiring reapplication. In addition, in the case of the ferrites, corrosion is an issue, particularly in the harsh environmental conditions out at sea. Furthermore, the ferrite-based RAM are relatively dense, and therefore add significant weight to the structure. The advent of conducting polymers has introduced viable alternatives to traditional RAM. Indeed there are a number of studies that indicate that conducting polymers have electromagnetic shielding and absorption properties. In addition, conducting polymers are relatively lightweight, corrosion-resistant, conductive materials which may be easily produced in large-scale at low-cost. Conducting polymers are organic in nature, thus interact favourably with matrix materials; this interaction results in excellent adhesion, thus a more robust material. Furthermore, the properties of conducting polymers may be tailored, rendering these materials more flexible than traditional RAM.

Principal Results

The aim of this research was to investigate several conducting polymers, including polyaniline, its derivatives and copolymers, and polypyrrole. Several polymers were synthesized under a variety of conditions and characterized to determine the effect of the conditions. The results of the investigation indicate that control over the desirable properties is possible, and that conducting polymers hold much promise as candidates for RAM.

Significance

These findings are of great significance, as the conducting polymers appear to be a superior alternative to traditional RAM. Conducting polymers are relatively cheap, corrosion-resistant, lightweight, and easily tailored to suit any application.

Future Plans

Future investigations include the determination of polyaniline (including derivatives and copolymers) properties as a function of synthetic conditions, and the fabrication of a device, either a coating, other polymeric blend, or coated fabric. This device will be tested to ascertain its performance as a radar absorbing device.

Huber, T., Saville, P., Edwards, D., 2003, Investigations into the Polyaniline and Polypyrrole Families of Conducting Polymers for Application as Radar Absorbing Materials. DRDC Atlantic TM 2003-005.

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Introduction

Les matériaux antiradar conventionnels comme les ferrites ou le noir de carbone souffrent de problèmes liés à leur intégrité. On ne peut les utiliser, à moins de les intégrer à une matrice. Or, à cause de leur mauvaise adhérence au matériau de la matrice, ils s'en détachent, ce qui nécessite leur renouvellement. En outre, l'environnement marin corrode les ferrites et les matériaux antiradar contenant des ferrites sont plutôt denses, ce qui alourdit beaucoup les structures. La mise au point de polymères conducteurs permettra de remplacer avantageusement les matériaux antiradar conventionnels. En effet, plusieurs études ont montré que les polymères conducteurs absorbaient les ondes radars et qu'on pouvait les utiliser pour le blindage électromagnétique. Qui plus est, ils sont assez légers, résistent à la corrosion et on peut facilement les produire en grande quantité et à faible coût. Puisque les polymères conducteurs sont des molécules organiques, ils se lient facilement aux matériaux de matrice, ce qui produit un matériau plus robuste. Finalement, leur utilisation est plus souple que celle des matériaux antiradar conventionnels, puisque l'on peut produire des polymères conducteurs avec les propriétés voulues.

Résultats principaux

Cette recherche avait comme objectif d'étudier plusieurs polymères conducteurs, notamment la polyaniline, ses dérivés et copolymères, ainsi que le polypyrrole. Nous avons synthétisé plusieurs polymères dans diverses conditions, et les avons caractérisés afin d'établir les effets de ces conditions. Nous avons découvert qu'il était possible de produire des polymères conducteurs avec des propriétés voulues, ce qui en fait des candidats prometteurs comme matériaux antiradar.

Importance des résultats

Ce résultat est très important. En effet, les polymères conducteurs semblent supérieurs aux matériaux antiradar conventionnels et constitueraient une bonne solution de remplacement. Peu coûteux, légers et résistant à la corrosion, ils peuvent s'adapter facilement à toutes sortes d'applications.

Travaux futurs

Lors de travaux futurs, nous déterminerons comment les conditions de préparation fixent les propriétés de la polyaniline (ainsi que de ses dérivés et copolymères), et nous fabriquerons un dispositif : un revêtement, un mélange polymérique ou un tissu enduit, qui fera l'objet d'essai d'absorption d'ondes radar.

Huber, T., Saville, P., Edwards, D., 2003, Investigations into the Polyaniline and Polypyrrole Families of Conducting Polymers for Application as Radar Absorbing Materials. DRDC Atlantic TM 2003-005.

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1. Introduction

Organic conducting polymers (also referred to as synthetic metals or intrinsically conducting polymers) are a novel class of electrically conductive materials whose electrical (and magnetic) properties are derived principally through their possession of extended π-conjugation. The presence of extensive conjugation in these materials reduces the energy difference between the HOMO/valence and LUMO/conduction bands (i.e. the band gap), essentially making them small band gap semiconductors[1]. This reduction in the band gap is not sufficient to achieve appreciable electrical conductivities, however. The highest observed conductivities are usually only achieved in doped polymers. The introduction of dopants induces perturbations in the electronic structure, resulting in the formation of charge carriers (electrons or "holes" depending on the type of dopant). These features of conducting polymers (low band gap, dopant induced charge carriers and conductivities intermediate between insulators and metals – see Table 1) lend themselves to description by the same physical models applied to inorganic semiconductors.

Organic conducting polymers typically exhibit some common characteristics. Owing to their extensive conjugation, they are conformationally quite rigid on a molecular scale, resulting in some less than advantageous macroscopic properties. Most conducting polymers are insoluble in all but the most pernicious solvents. High molecular weight polyaniline (PANI), for instance, is insoluble in most solvents but was seen to display limited solubility in *m*-cresol and concentrated sulfuric acid, whereas there is no indication in the literature that (doped) polypyrrole is soluble in any solvent. Organic conducting polymers also tend to be infusible (they do not melt) at temperatures below those required to degrade (pyrolize) the polymer. Additionally, these materials are usually extremely brittle and have other poor mechanical properties. All of these properties are presumably related to energetically favourable interactions between the π-systems of proximal chains. These interactions are of a greater magnitude than the majority of solvent/polymer interactions, explaining the insolubility. These interactions, when coupled with the elevated melting points inherent with most high molecular weight organic polymers, are presumably sufficient to explain the infusibility. Finally, since these intermolecular π-system interactions are highly anisotropic (and since the polymers synthesized in bulk are largely amorphous), there exist many potential fracture points, explaining some of the poor mechanical properties. Given all of these factors, conducting polymers can be exceedingly difficult to characterize by most conventional methods, and equally difficult to process from an applications standpoint.

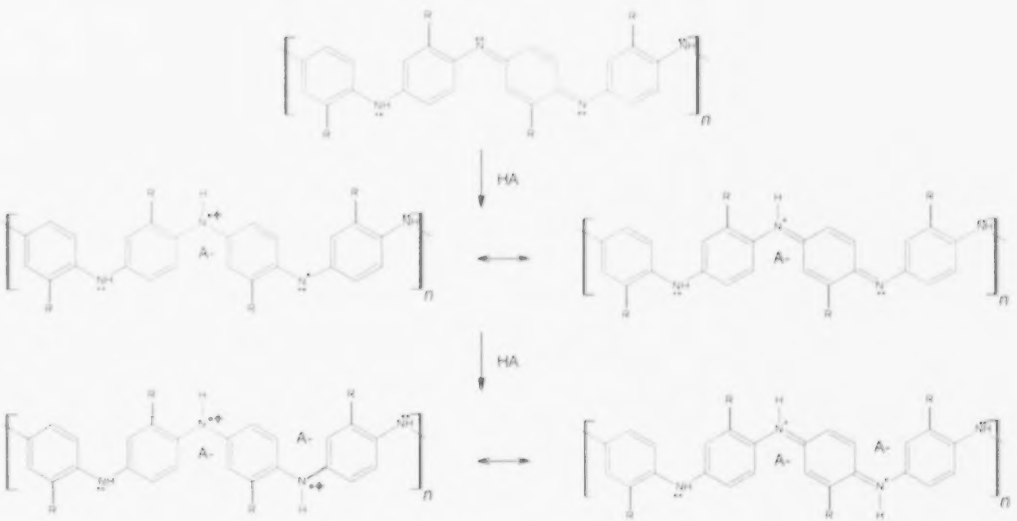
The specific work undertaken involved the investigation of two different "families" of conducting polymers: the polyanilines and the polypyrroles. Polyaniline, as well as copolymers of aniline and functionalised anilines (2-methylaniline, 2-methoxyaniline, 2-aminobenzoic acid, aniline-2-sulfonic acid, etc.), were synthesized in bulk through simple aqueous oxidation of monomer(s). Polyanilines, while subject to redox doping, can also be doped by protonic/Brønsted acids. This is a doping mechanism seemingly unique to the polyaniline family of conducting polymers, which, unlike redox doping, involves no change to the number of electrons present in the system. Instead, the protonation of imine sites present on the polymer stabilizes delocalised semiquinoid/benzenoid radical species, resulting in allowed electronic states between the HOMO and LUMO derived bands[1]. The choice of

protonic acid can presumably have significant effects on the conformational morphology of individual polymer chains (which are helical or coiled in solution[2]) as well as the packing of these chains, as evidenced by changes in the bulk conductivities.

TABLE 1: REPRESENTATIVE CONDUCTIVITIES FOR A VARIETY OF DIFFERENT MATERIALS[3]		
Material	Undoped Conductivity /S·cm^{-1}	(Doped) Conductivity /S·cm^{-1}
Gold, Silver, Copper	N/A	~ 10^{6}
Oriented, regioregular *trans*-polyacetylene / I_n^- (n=3, 5, 7, … , n)	~ 10^{-3} [4]	~ 10^{5} [5]
Polypyrrole / PTSA	~ 10^{-10} [6]	10^{-3} to 10^{2}
Polyaniline / HCl	~ 10^{-10} [5]	~10^{1}
Silicate Glass	N/A	~ 10^{-10}
Diamond	N/A	~ 10^{-14}
Quartz	N/A	~ 10^{-18}

Polypyrrole was also investigated, however in this case the synthetic method was electrochemical oxidation of monomer in an electrolyte containing dopant ions. The doping mechanism in the polypyrroles is not protonic, but instead is one of charge compensation. Polypyrrole in its (oxidized or "p-doped") conducting form is believed to consist of closely packed, linear poly(radical)cation chains, the anions present being associated with the polymer chains in order to maintain overall electroneutrality [6]. As with the polyanilines, the choice of dopant ion affects the morphology of the polymer, however the effect on these systems is probably related primarily to interchain packing, the conformations of the individual chains being more rigorously enforced by the bonding present. This bonding is best described by a mingling of nondegenerate aromatic and quinoid forms [7] (see Figure 2).

Conducting polymers have garnered a great deal of interest for use as radar absorbing materials (RAM), for a number of reasons. They often show abnormally high dielectric constants in the microwave region [3], indicating that they exhibit resonant absorptions/relaxation processes in this frequency domain. As well, the electrical conductivities of these materials can be carefully controlled through doping, presenting the possibility of designer RAM, which is to say RAM which can be "tuned" to absorb strongly over specific frequency domains [8]. There is also the enticing possibility of being able to produce conducting polymers, which are amenable to fabrication and processing using techniques already in place for other polymers. This offers the potential of effectively combining radar-absorbing characteristics with the utility and versatility of common plastics.



R = H, CH_3, OCH_3, CO_2H, SO_3H

Note: Spin and charge are actually delocalized over ~ 70 to 100 Å ^{o} at room temperature, corresponding to several repeat units

Figure 1: Illustration of Some of the Electronic States in Polyaniline(s) Developing on Protonic Acid Doping

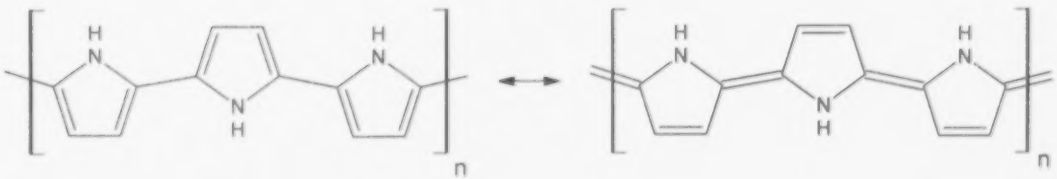


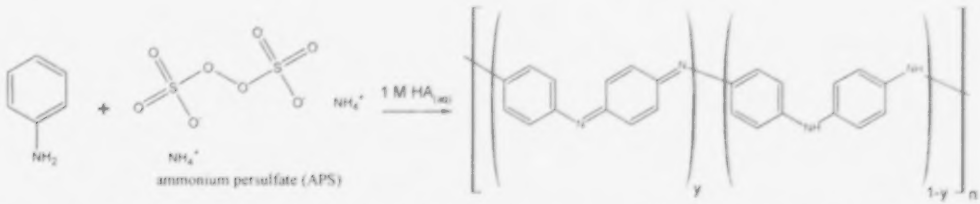
Figure 2: Aromatic and Quinoid Resonance in Polypyrrole

Although a great deal has been published on organic conducting polymers, very little information is available in the literature relating their synthesis and the physical properties required for useful radar absorbing materials (specifically their dielectric behaviour and electrical conductivities). As such, the scope of the work conducted was broad, consisting in large measure of varying a variety of synthetic parameters in an effort to ascertain their effects on these desired properties.

2. Experimental

2.1 Polyanilines (PANIs)

The general method used in the oxidative polymerization of aniline (and of substituted anilines) was to prepare separate aqueous solutions of oxidant and monomer in concentrated (1 M) dopant acids (See Figure 3). A small amount of N-phenyl-1,4-phenylenediamine ("dianiline," the dimer of aniline, which is more readily oxidized than aniline) would typically also be included in the monomer solution to act as an initiator. The oxidant solution would slowly be added to the monomer solution resulting in the rapid formation of an opaque suspension of intensely coloured (usually blue/black or dark green) polymer. This colour change was frequently accompanied by a large increase in viscosity (gel formation) and by the evolution of considerable heat. The solution/suspension would be stirred for a prescribed time period at a constant temperature before being filtered through a glass frit. The bulk polymer was thoroughly retained by the frit, while the filtrate was generally colourless or pink, the colouration being ascribed to the presence of soluble oligomeric reaction products. Cleaning of the product was accomplished by rinsing with water, followed by acetone, drying, grinding, and rinsing again until no trace of colour could be observed in the acetone rinse. Much of this effort was to remove soluble oligomers and to minimize the presence of toxic species in the final polymer, such as residual aniline, dianiline, and benzidines (biphenyl-4,4'-diamines).



Note that the polymer produced in excess acid is protonated to varying degrees (emeraldine salt) and will have associated counter-ions. Additional major products (from the APS), which are not shown, are ammonium sulfate, and ammonium bisulfate.

Figure 3: Typical Aniline Polymerization

Aside from the bulk synthesis of PANIs, a variety of other procedures were attempted. A few of these procedures involved the preparation of PANI in the presence of some other soluble polymer to form composite materials *in situ*. This was attempted with both aqueous and organic solvent systems. Aqueous syntheses along these lines employed water soluble polymers such as poly(vinyl pyrrolidinone) (PVP) and poly(vinyl alcohol) (PVA), while those employing organic solvents were conducted using reverse (water in oil) emulsions in which the monomer was dissolved in xylenes along with polystyrene or poly(methyl methacrylate) (PMMA) with the oxidant (APS) supplied in an aqueous solution. These methods were not particularly successful largely due to problems associated with cleaning the resultant products. Another area investigated with regards to *in situ* composite formation was the synthesis of

PANI in the presence of carbon nanotubes. The as prepared commercial nanotubes were dispersed in a surfactant solution by way of ultrasonic agitation, followed by the addition of monomer and oxidant, producing a composite material.

The development of composite materials containing polyanilines is of great importance in order to help compensate for the some of the disadvantageous properties of the bulk polymers. Dielectric measurements required samples of very specific dimensions, the precision required unobtainable using the polymer as prepared. A method was developed for the preparation of composites in which bulk PANI, PMMA and a plasticizer were compression molded at temperatures above the glass transition of PMMA (~120 °C) and at pressures of about 80 psi. The plaques produced had greatly improved mechanical properties and could be milled to the required dimensions. In addition, they retained some electrical conductivity, usually proportional to the amount and bulk conductivity of the conducting polymer used. Some preliminary investigations into the optimal conditions for the preparation of these composites (temperature, plasticizer, and proportion of conducting polymer) were also conducted, the success of these efforts being gauged by conductivity measurements and dielectric spectra.

2.2 Polypyrrole

The method employed for the production of polypyrrole was electrochemical (specifically galvanostatic), in which thin (<0.5 mm) polymer films were grown from monomer/dopant solutions onto stainless steel working electrodes. The conditions varied for these reactions were principally the dopant ion (type and concentration), the reaction time, and the pH of the electrolyte. The dopants employed were essentially those used for the polyanilines, but also included sodium salts of 1- and 2-naphthalenesulfonic acids (1- and 2-NSA) and 1,5-anthraquinonedisulfonic acid (AQDSA). Other synthetic conditions, including the monomer concentration, temperature and the applied current, were held constant based on optimum values described in the literature [4,10-12]. Several other areas were also explored in a preliminary fashion, including the use of fabric chemically coated in polypyrrole as the working electrode as well as the possibility of electrochemically cycling the films in order to modify the doping level/electrical conductivity.

The general procedure employed was to prepare a solution of pyrrole and dopant ion. In the case of dopants supplied in their acid forms, the pH was varied using aqueous sodium hydroxide. The monomer/dopant solution would then be chilled to 1°C in an environmental chamber. The electrodes would were then assembled – a stainless steel plate as the anode and a stainless steel mesh as the cathode – and a current of about 3 mA/cm^2 supplied. A general mechanism for this reaction is illustrated in Figure 4. The films produced were black and quite resilient, and could be fairly easily peeled from the electrodes. Films were then mounted in cards for IR characterization, or were cut and mounted on thin plastic blocks of the appropriate dimensions required for dielectric characterization. Conductivity data could readily be acquired using either sample configuration.

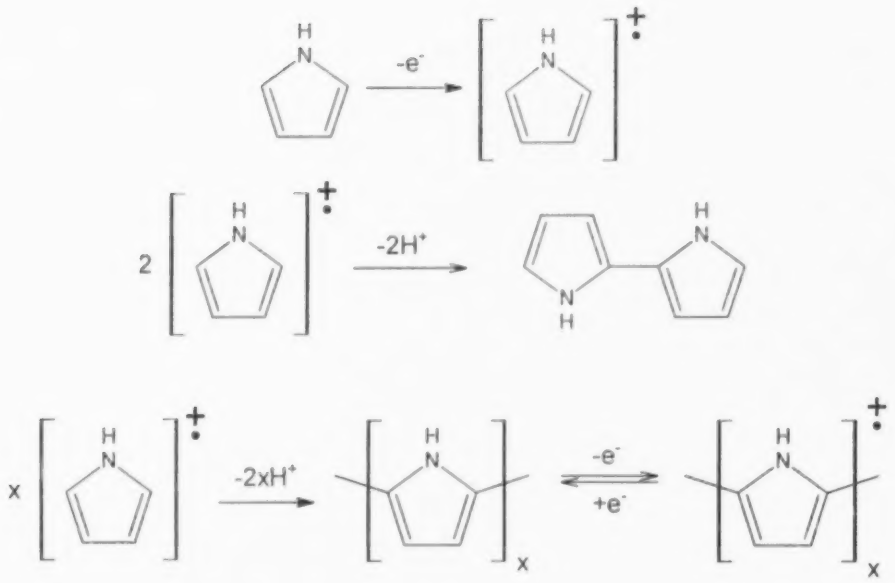


Figure 4: General Mechanism for the Oxidative Polymerization of Pyrrole

2.3 Characterization

Many polymeric systems can be troublesome to characterize – conducting polymers have a variety of properties, which make their description particularly problematic. Characterization of molecular weights in many polymers can be accomplished by way of gel permeation chromatography (GPC). The main requirement of this method is that the polymer be completely soluble in some solvent. Conducting polymers are typically insoluble in virtually every solvent, with the most effective solvents being extremely unpleasant and still only capable of producing dilute solutions of low molecular weight fractions. As such, highly useful information, such as any relationship between synthetic conditions and the molecular weight and molecular weight distribution of the polymer is extremely difficult to obtain. For both polyaniline and polypyrrole systems the true yield cannot be determined directly, but must involve removal of associated dopant. Other methods used to characterize bulk polymers are only marginally applicable to conducting polymers. Thermal analysis by differential scanning calorimetry (DSC), which can often be used to determine the glass transition temperatures and the crystallinity of polymers, is uninformative for conducting polymers generally as they tend to exhibit no definitive features below their decomposition points [13]. X-ray diffraction studies of these materials are also relatively uninformative, with the general result being that the high molecular weight polymers are largely (>50%) amorphous [14].

All the difficulties associated with physically characterizing these systems aside, some methods were available to help reveal the nature of the polymers produced. Attempts were made to correlate the oxidation state of polyaniline (as assumed from the amount of oxidant

used in the synthesis) with IR peaks assigned to benzenoid and quinoid carbon-nitrogen bonds. Polypyrrole films were examined in the far-, mid-, and near IR to examine the effects of synthetic conditions on the presence of a broad absorption characteristic of intraband electronic transitions (i.e. free-carrier absorptions [1]). Some polyanilines were also characterized by ^{1}H NMR spectroscopy, although the utility of this method was fairly limited. Only polyaniline and some copolymers containing appropriate functionality (i.e. 2-methylaniline/aniline and 2-methoxyaniline/aniline copolymers) provided meaningful results. The conducting (protonated) forms of these polymers are paramagnetic (and insoluble), making the dedoping of the polymer a requisite. Fortunately, the dedoped polymers are somewhat soluble in DMSO, allowing spectra to be acquired. Despite dedoping, spectra obtained from copolymers containing carboxylic or sulfonic acid functionality showed very broad (5-10 ppm) peaks, presumably due to this paramagnetism (and perhaps exchange with residual water in the solvent).

2.4 Conductivity

The primary means of characterizing all the polymers produced was through conductivity measurements. This is of interest from a RAM perspective inasmuch as there is a loss mechanism through which ohmic heating of resistive (slightly conductive) materials results in the dissipation of incident radiation as heat [15]. Sample preparation for the bulk polymers involved pressing the cleaned and dried polymer in a pellet press. About 200 mg of sample was used which, when pressed at a constant pressure with a hydraulic press, produced circular pellets of about 16 mm in diameter and ~1 mm in thickness. The films produced could be measured without further preparation. The measurement of DC conductivities was accomplished through use of the 4-probe van der Pauw technique [4]. By this method, four highly conductive metal probes (gold coated in the apparatus used) are placed in line; current is injected and collected through the two outermost probes, while the potential drop between the two inner probes is monitored (see Figure 4). Where contact was poor, a small quantity of graphitic paint was applied to the probe tips. The probe was then positioned on the sample usually giving good contact on drying of the paint.

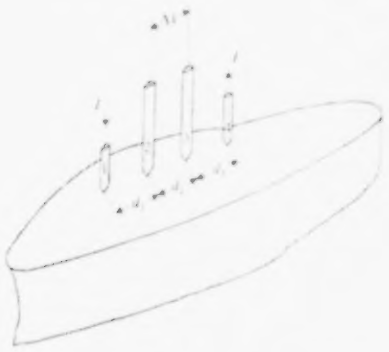


Figure 5: Schematic Illustration of the setup for 4-Probe Conductivity Measurements

2.5 Dielectric Spectroscopy

A method was developed in parallel with the synthetic work in order to measure the dielectric properties of the materials produced in the X band (~8 to ~12 GHz). [16] The dielectric spectra collected over this frequency range were critical in gauging the radar absorbing properties of the materials produced. Although the specific details of the method are not relevant to this report, some of the theory behind dielectric spectroscopy (and the dielectric response of materials) is useful. The dielectric constant (or permittivity – ε^*) of a material is a complex, frequency dependent quantity, which is related to the way in which the material responds to an applied electromagnetic field. Although the physical mechanism(s) responsible for the dielectric response varies depending on the frequency domain, the intensity of the absorption (i.e. the absorption coefficient) at a given frequency can be related to the imaginary component of the complex dielectric constant through Equation 1,

$$K(\omega) = \frac{\omega \cdot \varepsilon''(\omega)}{n_r(\omega) \cdot c} \tag{1}$$

where $K(\omega)$ is the frequency dependent absorption coefficient, ω is the frequency of interest, $\varepsilon''(\omega)$ is the frequency dependant imaginary dielectric constant, $n_r(\omega)$ is the (frequency dependent) real part of the refractive index of the material, and c is the speed of light. This relationship between the absorption coefficient and the dielectric constant strictly holds only for non-metals, the situation in metals being dominated by reflection rather than absorption or transmission. The dielectric spectra obtained consisted of the real and imaginary permittivity, plotted as a function of frequency. A useful parameter derived from these spectra was the dielectric loss tangent, tan δ_e, which is the ratio of the imaginary part to the real part of the dielectric constant. This loss tangent can be interpreted as a measure of the amount of energy dissipated relative to the amount stored. For radar absorbing materials, it is desirable to maximize this loss tangent in the frequency range of interest.

3. Results

3.1 Polyanilines

Several series of experiments were conducted in order to assess the effects of a variety of reaction conditions on the production of polyaniline. One such series involved varying the ratio of oxidant to monomer. Four ratios (1:4, 1:2, 3:4, and 1:1) were employed using HCl as the dopant. Although a clear trend was observed in the polymer yield (see Figure 6), no consistent trend with respect to the conductivity was observed.

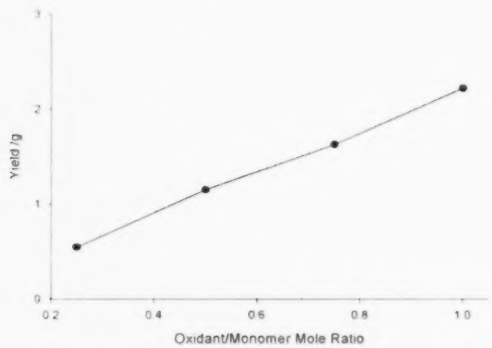


Figure 6: Yield of PANI/HCl Made Using Different Monomer/Oxidant Ratios

Another series of syntheses was conducted in which the only parameter varied was the nature of the dopant acid. Although the highest electrical conductivities were observed for HCl doped PANIs (see Figure 7) the use of a volatile dopant has further implications. One of these is an observed drop in conductivity over time (see Figure 8) or on drying *in vacuo*. Additionally, the relative ease with which HCl is lost has a deleterious effect on any metal equipment used in the processing of the bulk polymer. Indeed, corrosion was observed on metal surfaces used in pressing pellets or in compression molding of HCl doped polymer. Yields for the different doped PANIs are difficult to compare directly, given that the amount of dopant associated with the polymer may well vary with the nature of the dopant.

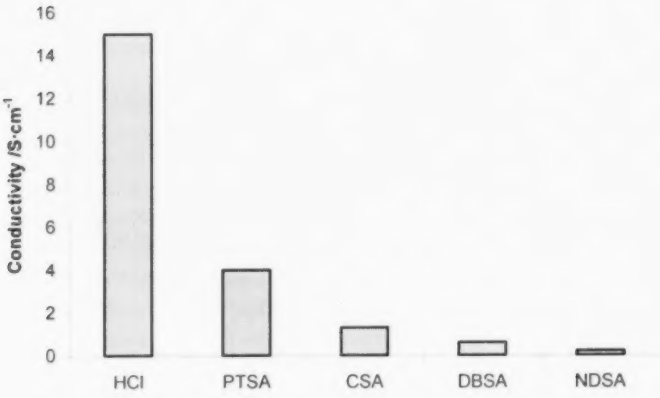


Figure 7: Representative Conductivities of Polyaniline Doped Using a Variety of Acids

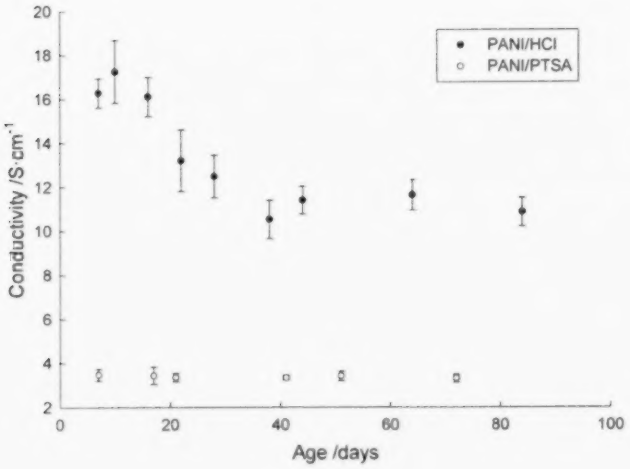


Figure 8: Conductivity Over Time for PANI/HCl vs. PANI/PTSA

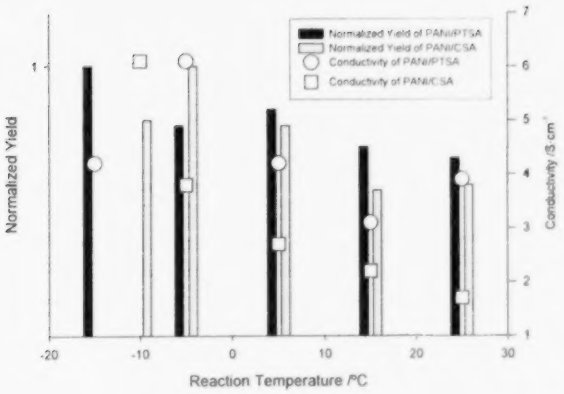


Figure 9: Trends in Yields and Conductivities for PANI/PTSA and PANI/CSA Synthesized at Different Temperatures

Still another series of experiments employing several different dopant acids was conducted in which the reaction temperature was controlled in an environmental chamber. The effects of temperature varied with the dopant employed; PTSA doped PANI seemed relatively unaffected by temperature both in terms of yield and conductivity, while CSA doped PANI showed an appreciable increase in both yield and conductivity as the reaction temperature was reduced (see Figure 9).

Several patents describe the use of dianiline as useful in improving yields and reducing induction times [17,18], thus dianiline was included in the majority of syntheses. Subsequent investigation into the effects of dianiline was undertaken, in which the amount used was varied. The yields of polymer generally increased with the amount of dianiline used, however (not surprisingly) large amounts of dianiline resulted in an increase in the amount of acetone soluble reaction products (oligomers). The conductivity of PANI/HCl synthesized using dianiline had lower conductivities than those synthesized without (see Figure 10). Given that the yields obtained were not hugely different, even after relatively short reaction times (~4 hours), this suggests that the use of dianiline is not necessary, if the conductivity of the product is to be maximized. However, the presence of dianiline may favourably affect the polydispersity and reproducibility.

A number of copolymers in the polyaniline family were also prepared. The yields of the various copolymers also do not readily lend themselves to comparison inasmuch as not only is the degree of dopant association not known, but the relative amounts of monomer incorporated into the polymers are also unknown. ^{1}H NMR spectra were somewhat informative determining the relative incorporation of monomers for polymers containing amenable functionality, but were not universally (or unambiguously) applicable. Despite the difficulties in assessing the molecular structure of these copolymers, trends in their conductivities in relation to the relative amount of aniline/substituted aniline employed were observed (see Figure 11).

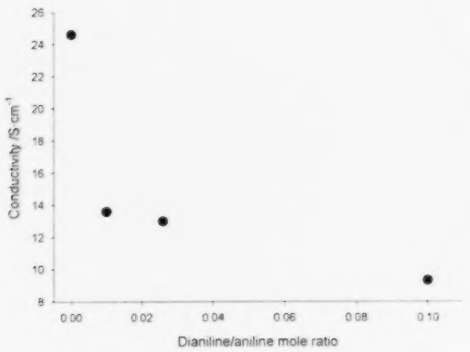


Figure 10: Conductivity of PANI/HCl Synthesized Using Varying Amounts of Dianiline

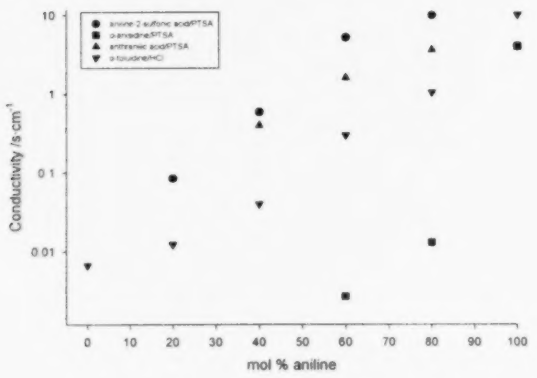


Figure 11: Conductivity of the Mole % Aniline in Several Series of Copolymers

3.2 Polyaniline Composites

As previously mentioned, a method was developed in which PANIs were incorporated into composites by way of compression molding. The temperature at which the composites were prepared was found to have a considerable effect on their conductivity, an order of magnitude reduction being observed on the increase of the processing temperature from 150°C to 180°C. The amount of plasticizer (hydroquinone) was also observed to have a considerable effect on conductivity. Neither of these parameters were extensively investigated, however, the

temperature being difficult to control using the compression molder used and the optimum amount of plasticizer being available from the literature [13]. The conductivities of the composites were related to the amount of conducting polymer present (see Figure 12), approaching the limiting value expected from the bulk polymer. The loss tangents of the composites showed an apparent linear increase with the amount of conducting polymer present (see Figure 13).

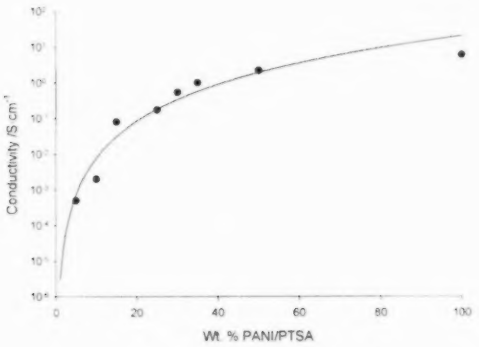


Figure 12: Conductivity of PANI/PMMA Plaques as a Function of PANI Loading

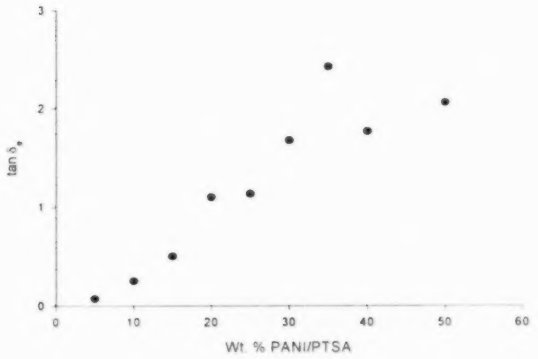


Figure 13: Loss Tangent (10 GHz) at Different Levels of PANI/PTSA Loading

3.3 Polypyrrole

The effect of dopant type and concentration on the conductivities of polypyrrole films was extensively investigated. All dopants investigated showed a similar relationship between concentration and conductivity – this relationship is illustrated for two dopants in Figure 14. High conductivities were observed for high dopant concentrations with all apparently approaching limiting values at high dopant levels (~0.1 M). The mechanical properties of the films also improved with the doping level/conductivity. Although all films could fairly easily be removed from the electrodes, lightly doped films were very brittle and tended to crack and chip, whereas the highly doped films were flexible, pliable, and quite resilient. A linear relationship between film thickness and reaction time was observed for a series of PTSA doped films, which also appeared to hold regardless of dopant. Some deviations from linearity were observed, but were generally consistent with differences in surface morphology (such as tubular or nodular structures protruding from the surfaces of the films) rather than true film thickness. Electrochemical deposition/graft polymerization onto fabric chemically coated with polypyrrole was successful, however not reproducibly, given difficulties in obtaining consistent current densities through the fabric electrodes. Cycling of the films was also attempted, however the result of the oxidative portion of the cycle was typically degradation the film, with a loss of both mechanical properties and of electrical conductivity. This may be consistent with the changes in free volume associated with doping (increase in free volume) and dedoping (decrease in free volume). This free volume change is believed to arise from Coulombic repulsions between chains as they are oxidized to their cationic form [19], and the reverse process taking place on reduction. This expansion and contraction of the films on cycling may well account for their mechanical failure. Most of the films produced were highly conductive, so much so in fact that their dielectric behaviour was essentially metallic, with reflection rather than absorption or transmission dominating over the frequency range investigated.

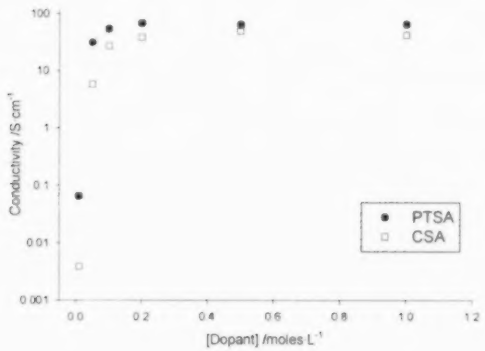


Figure 14: Conductivity as a Function of Dopant Concentration for Electrochemically Synthesized Polypyrrole Films

4. Discussion and Recommendations

The synthesis of polyaniline(s), although simple in practice, does not necessarily give completely reproducible results for the same set of reaction conditions. Variations in conductivities and yields were observed that were not readily explicable. This is exacerbated by the lack of other applicable characterization techniques, such as molecular weight characterization. Reproducibility issues aside, a great deal of progress was made in the property directed synthesis and post-synthetic processing of the polyanilines. The development of a means for producing PANI composites was critical in measuring their dielectric properties, no ready means being previously available. Although this represents a step forward in determining the radar absorbing properties of these materials, additional work is still required to further assess the effects of the conditions used in the preparation of these types of composites. Further investigation might include varying the type of matrix polymer (only PMMA was employed in the work conducted), the plasticizer, both type and proportion (the "best" plasticizer and concentration used were obtained from the literature [13]), as well as the temperature and pressure used in the compression molding (also both obtained from the literature).

The apparent monotonic increase in loss tangent with PANI loading is interesting, but ambiguous as to its origin. Given the absence of a similar trend in conductivities, the relaxation/loss mechanism may well occur as a result of the heterogeneity of the material. It is recognized that conductive inclusions may result in resonant absorption when they have dimensions on the same order as the wavelength of the incident radiation [15]. If this is the case, it will be difficult to disentangle this effect from any arising from the conducting polymer itself. Further experiments on these systems need to take such possibilities into account, for in the absence of significant contributions to the loss arising from the conducting polymer the same radar absorbing characteristics could likely be obtained more easily using other conductive materials such as metal or carbon particles incorporated into an insulating matrix.

The polypyrrole films, although reproducible in terms of conductivity, also likely require a great deal of further work to produce radar absorbers of practical utility. The highly conductive films, as mentioned, are too reflective to be of particular use as radar absorbers. It is unfortunate that the mechanical properties of these films become less favourable as their level of doping/conductivity decreases, given that these display better absorption characteristics. Regardless, it is difficult to envision a process through which such films could be practically applied. The mechanical properties, while adequate for handling in a laboratory setting, are insufficient to withstand real environmental stresses.

It is perhaps ironic that the features that make conducting polymers potentially useful radar absorbers (i.e. their conductivities) are coupled with other features that make them extremely difficult to characterize and apply in a meaningful way. Nonetheless, the work conducted was of some value, inasmuch as a broad survey of the ways in which the conditions used in producing these materials effects their desired properties is a necessary step in developing a useable product. There is still a great deal of potential for polyanilines and polypyrroles as radar absorbers, given that their properties can be controlled and optimized through the

conditions employed in their synthesis, as well as through post-synthetic processing. There is, however, much further work required to develop a thorough understanding of the ways in which conducting polymers can be optimized and applied as practical radar absorbing materials.

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APS	ammonium persulfate
AQDSA	1,5-anthraquinonedisulfonic acid
cm	centimeter
CSA	camphorsulfonic acid
°C	degrees Celsius
DBSA	dodecylbenzenesulfonic acid
DC	direct current
DMSO	dimethyl sulfoxide
DND	Department of National Defence
DSC	Differential Scanning Calorimetry
ε^*	complex permittivity
ε'	real permittivity
ε''	imaginary permittivity
GHz	gigahertz
GPC	Gel Permeation Chromatography
^1H	proton
HCl	hydrochloric acid
HOMO	highest occupied molecular orbital
IR	infrared
LUMO	lowest unoccupied molecular orbital
M	molar, moles/litre
mg	milligram

mm	millimeter
n	refractive index
NDSA	naphthalenedisulfonic acid
NMR	nuclear magnetic resonance
NSA	naphthalenesulfonic acid
PANI	polyaniline
PMMA	polymethyl methacrylate
ppm	parts per million
psi	pounds per square inch
PTSA	para-toluenesulfonic acid
PVA	polyvinyl alcohol
PVP	polyvinylpyrrolidinone
RAM	radar absorbing material(s)
S	Siemen (ohm^{-1})
tan δ_e	dielectric loss tangent

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The synthesis and characterization of two families of conducting polymers, namely polyaniline and polypyrrole, were investigated in order to ascertain their viability as radar absorbing materials (RAM). A large number of polyanilines (including derivatives and copolymers) were synthesized by chemical oxidative polymerization, while the polypyrroles were produced by electrochemical oxidation. The syntheses were performed under varying reaction conditions (variable temperature, time, dopant, oxidant/monomer ratio) to investigate the effects of the synthetic parameters on the conductivity and permittivity of the resulting polymers. The conductivity of the polymers was measured using the four point probe method at ambient temperature. In the case of polyaniline, the samples were either pressed pellets of the bulk polymer or polyaniline/acrylic composites, whereas the polypyrrole samples were in the form of thin films. The complex permittivity of the polymers was determined from the reflection parameters measured across the X-band (8 - 12 GHz) in the microwave region of the electromagnetic spectrum. The data indicate that the synthetic parameters investigated, do indeed have an effect on the morphology of the polymers, and thus on the conductivity and permittivity.

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